

# Structure–Property Characteristics of Pyrolytic Lignins Derived from Fast Pyrolysis of a Lignin Rich Biomass Extract

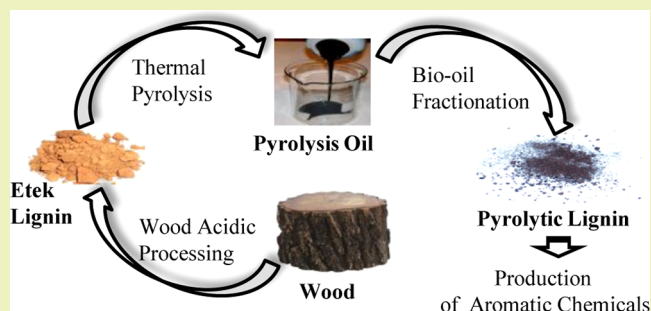
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**ABSTRACT:** In this work, pyrolytic lignins isolated from the liquid product of the fast pyrolysis of Etek lignin were characterized using various analytical techniques. This is necessary to evaluate their potential usefulness as an aromatic chemical feedstock in a biomass pyrolysis scheme. Pyrolytic lignins were separated into various fractions by their solubility in water and dichloromethane. Results revealed that the thermal pyrolysis yielded lignin fractions of higher oxygen and lower carbon and hydrogen contents, leading to a decrease in their heating values. Pyrolytic lignin fractions were decarboxylated, had a higher concentration of aryl and alkyl hydroxyl moieties, and were lower molecular weight than the starting lignin. TGA analysis indicates that the pyrolytic lignins begin to thermally degrade at 120 °C. Overall the characterization data suggests that pyrolytic lignins obtained from the fast pyrolysis of Etek lignin are potentially useful feedstocks for sustainable production of renewable aromatic chemicals.

**KEYWORDS:** Etek Lignin, Fluidized Bed Fast Pyrolysis, Pyrolysis Oil Upgrading, Physicochemical Properties, Value-Added Chemicals



## INTRODUCTION

Lignin is a cross-linked phenylpropanoid polymer arising from radical coupling reactions of three primary precursors, monolignols *p*-coumaryl, coniferyl, and sinapyl alcohols, producing a high-molecular-weight polydispersed matrix.<sup>1,2</sup> The cross-linked C<sub>9</sub> phenol units are attached mainly through C–O–C bonds, and some (30%) are connected through C–C linkages. Lignin composition is generally characterized by the relative abundance of *p*-hydroxyphenyl (H), guaiacyl (G), and syringyl (S) units, derived from each of the three monolignols (vide supra) and by the distribution of inter-unit linkages in the polymer (e.g.,  $\beta$ -aryl ether;  $\beta$ -O-4, phenylcoumaran;  $\beta$ -5, resinol;  $\beta$ - $\beta$ , biphenyl; 5–5, diphenyl ether; 4-O-5). Two main classes of this biopolymer are distinguished, namely, the guaiacyl type lignin (typical of conifers) and the guaiacyl-syringyl type lignin, which is formed in deciduous plants.<sup>3</sup> Herbaceous species produce lignins with higher concentration of *p*-hydroxyphenyl (H) units. Lignin samples from Etek are the residue of acidic processing of woods to produce fermentable sugars (used to produce ethanol). Raw Etek lignin contains approximately 45.7% cellulose and 29.2% lignin, with extractives, hemicelluloses, and ash. Its structure is altered from natural lignin, but it still contains polyphenols and could be a potentially useful source of aromatics for the chemical industry. The focus of our study is how pyrolysis affects the lignin fraction, so the raw Etek lignin was extracted to produce pure lignin before pyrolysis was conducted. Like biomass, the

products of its thermal pyrolysis may provide an important component of the modern biorefinery scheme, offering nonpetroleum-based starting materials for unique routes to various fine and bulk chemicals.

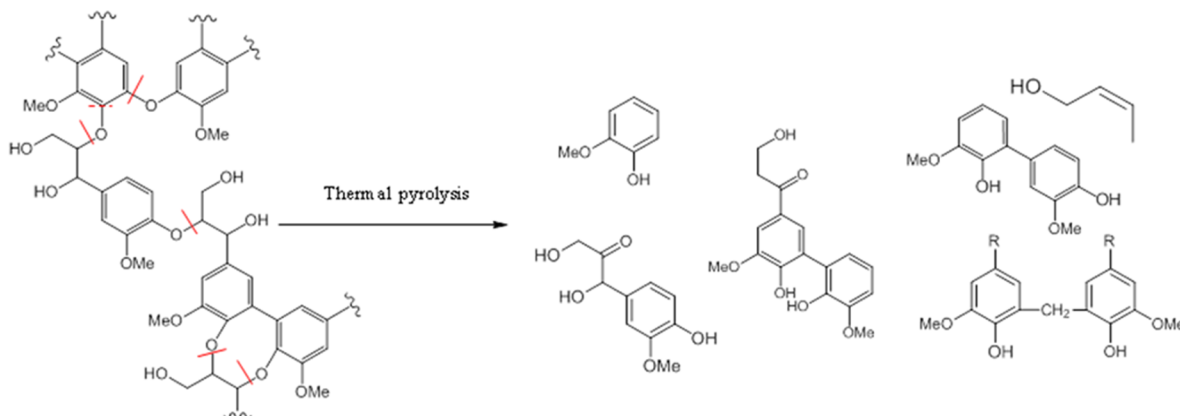
Given the molecular structure and wide availability of lignin, it is a potentially transformative feedstock if an economic conversion into valuable materials, for example, chemicals and/or high-octane fuel additives, can be developed. As a result, various promising conversion routes of lignin into chemicals and fuels are being investigated; among them catalytic and noncatalytic routes that include thermochemical, chemical, and biological processes have been reported.<sup>4–9</sup>

Fast pyrolysis of lignin has been heavily studied as a method of forming valuable chemicals or hydrocarbon fuels.<sup>10–13</sup> The resulting pyrolysis oil (PO) is a dark product with a large number of oxygen-containing functional groups in which pyrolytic lignin (PL) is a major component adding complexity and viscosity to the liquid mixture. Therefore, water-fractionating PO in order to extract the PL could be an important unit operation in a biorefinery scheme. PL (a sum of lignin fragments of different molecular weights) can be solvent fractionated into chemically different fragments, which can be further used as different chemical intermediates. Characterizing

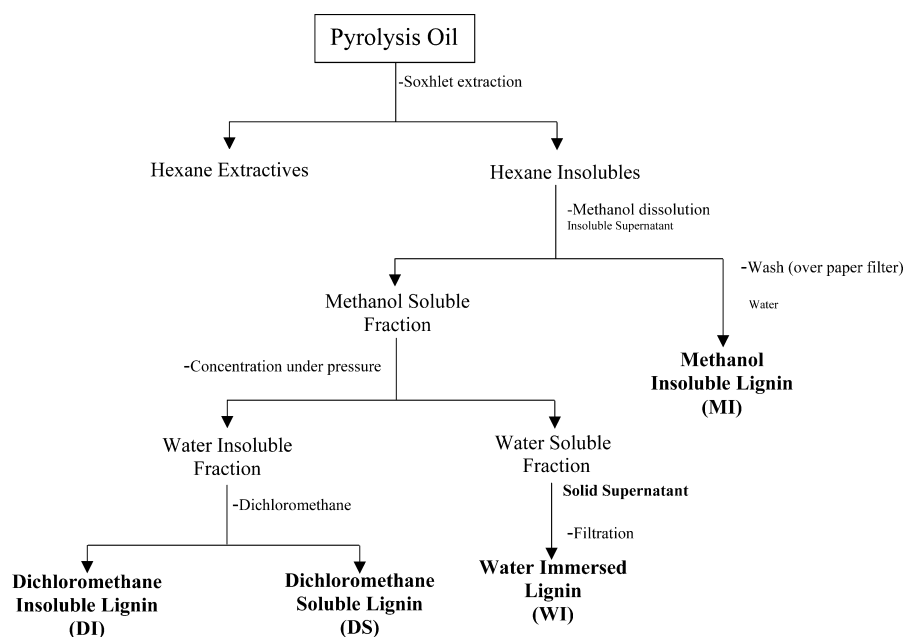
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Scheme 1. Suggested Pathways of the Thermal Pyrolysis of Guaiacyl-Type Lignin<sup>16,17</sup>

Scheme 2. Flow Chart of Isolation and Fractionation of Pyrolytic Lignins



the thermally degraded lignin is important to determine what end-use the extracted product is suitable for and thus promote its industrial use as a feedstock for the production of value-added chemicals.

In this work, extracted and fractionated PLs from pyrolysis oil obtained by fast pyrolysis of Etek lignin (EL) have been characterized. For comparison purposes, nonthermally altered lignin was extracted directly from the commercial EL precursor for use as the control lignin versus which various properties of PLs were evaluated. All extracted lignin fractions were characterized in terms of their elemental composition, heating values, functional groups, esteric bonds, molecular weight distribution, surface morphology, and thermal stability. The overarching goal was to produce various PL fractions by solubility differences and evaluate their physicochemical properties for their efficacy as chemical intermediates.

## MATERIALS AND METHODS

**Fast Pyrolysis of Etek Lignin.** The Etek Lignin provided by SEKAB E-Technology Corporation (Örnsköldsvik, Sweden) was obtained as a residue of the acidic (dilute sulfuric acid) processing of wood to produce fermentable sugars (organosolv

process). The solid residue was water-washed and neutralized prior to being dried and packed as a commercial product. Fast pyrolysis of Etek lignin was carried out in a bubbling fluidized bed of quartz sand at temperatures of  $\sim 500$  °C with a residence time of  $<1.0$  s. The reaction system has been described in previous reports.<sup>14,15</sup> The system comprised a 7.5 cm (3 in.) diameter fluidized bed reactor section, followed immediately by a cyclone to remove biochar. Pyrolysis vapors were condensed by a series of four condensers cooled by cold water ( $\sim 4$  °C); the remaining aerosols were collected by electrostatic precipitators (ESP). The ESP fraction of the pyrolysis oil typically contains most of the aerosols and pyrolytic lignins and hence was the fraction that was used for isolation of the pyrolytic lignin described in this work. The suggested thermochemical conversion reactions occurring during the lignin pyrolysis are summarized in Scheme 1.<sup>16,17</sup>

**Isolation and Fractionation of Pyrolytic Lignins.** In order to isolate pyrolytic lignins from the liquid pyrolysis product, the pyrolysis oil was mixed with sand and loaded in a porous cellulose thimble. As summarized in Scheme 2, Soxhlet extraction ( $70 \pm 1$  °C) was performed with hexane to remove most nonpolar compounds contained in the pyrolysis oil. Then,

**Table 1.** Yield, Elemental Composition (wt%), and Heating Values of Isolated Lignins

lignin sample	yield (%)	C	H	N	S	O <sup>a</sup>	HHV (MJ/kg)
EEL	12.0	65.0	7.08	0.09	0.00	27.8	27.2
MI lignin	17.2	43.1	3.32	0.24	0.00	53.3 <sup>b</sup>	9.75
WI lignin	27.7	63.0	5.43	0.39	0.00	31.2	23.5
DI lignin	49.8	63.0	5.76	0.28	0.00	31.0	22.7
DS lignin	5.30	65.1	6.28	0.15	0.00	28.5	26.0

<sup>a</sup>By difference. <sup>b</sup>Includes oxygen and inorganics.

the remaining cake (made of sand and non hexane-extractable components) was extracted with methanol under shaking. The supernatant was filtered through Whatman filter paper No. 3. The residue was washed with methanol to yield the methanol insoluble (MI) fraction. The filtrate was mixed with water to yield the two main fractions: water-soluble (aqueous) and water insoluble (solid). The water insoluble fraction was mixed with dichloromethane yielding both dichloromethane soluble (DS) and insoluble (DI) fractions. Particles in suspension in the water-soluble fraction were separated by filtration producing the so-called water immersed (WI) lignin. After soaking on dry ice with methanol, the extracted lignins were subjected to an extensive freeze-drying under vacuum (overnight) to yield fine powders called pyrolytic lignins. The products were stored in desiccators over P<sub>2</sub>O<sub>5</sub> prior to further studies.

#### Extraction of Lignin from the Commercial Etek Lignin.

Lignin was extracted from the commercial Etek lignin that also contained carbohydrates. The commercial product was extracted with THF by stirring 10 g of Etek feedstock in 150 mL of THF at 45 °C for 2 h and repeated 3 times. After filtration the THF extract was concentrated under vacuum before it was added dropwise to water under stirring that caused precipitation of the lignin. The precipitate was filtered, washed with water, dried in a vacuum oven over P<sub>2</sub>O<sub>5</sub> at 65 °C for 5 h, and stored in a desiccator.

**Elemental Analysis and Heating Value.** Elemental analysis for carbon, hydrogen, nitrogen, and sulfur was carried out with a FLASH EA 1112 Series CHNS-O Analyzer (Thermo Electron Scientific, Madison, WI, U.S.A.) equipped with Eager 300 Software. The oxygen content was calculated from the C, H, and N difference as follows: O wt% = 100 - [C wt% + H wt% + N wt%]. The heating value was calculated according to the Dulong's formula,<sup>18</sup> i.e.,

$$\text{HHV (MJ/kg)} = \left[ 338.2 \times \%C + 1442.8 \times \left( \%H - \frac{\%O}{8} \right) \right] \times 0.001$$

**ATR-FTIR Spectroscopy.** FTIR spectra were obtained with a Platinum ATR-FTIR spectrometer ALPHA (Bruker Optics, Inc., Manning Park Billerica, MA, U.S.A.) equipped with intuitive OPUS 7.0 mentor software and a deuterated triglycine sulfate (DTGS) detector at a resolution of 4 cm<sup>-1</sup> with 32 scans for each sample. The spectra were collected using a diamond probe in the wavenumber range of 4000–525 cm<sup>-1</sup>.

**Quantitative <sup>31</sup>P NMR Analysis of Phosphitylated Lignins.** To perform the <sup>31</sup>P NMR analysis of the phosphitylated lignins, 30 mg of dried samples were accurately weighed and dissolved in a solvent mixture (0.50 mL) made of anhydrous pyridine and deuterated chloroform (1.6:1.0, v/v) containing a relaxation agent (chromium(III) acetylacetonate) and a phosphitylation reagent (2-chloro-4,4,5,5-tetramethyl-

1,3,2-dioxaphospholane, ~0.05–0.10 mL). The vial was capped and stirred for 60 min at room temperature. The reaction mixture was transferred into a NMR tube. Following an established procedure,<sup>19</sup> the quantitative <sup>31</sup>P NMR spectrum was acquired in the range of ~160–120 ppm using a relaxation delay of 5 s with 1000 transients to ensure a high signal/noise ratio. Chemical shifts and integrals were calibrated to an internal standard (phosphitylated N-hydroxynaphthalimide) that has a sharp peak at 152.2 ppm. Experiments were performed in duplicate. Each spectrum was integrated twice, and the amounts of different functional groups were calculated as described elsewhere.<sup>20,21</sup>

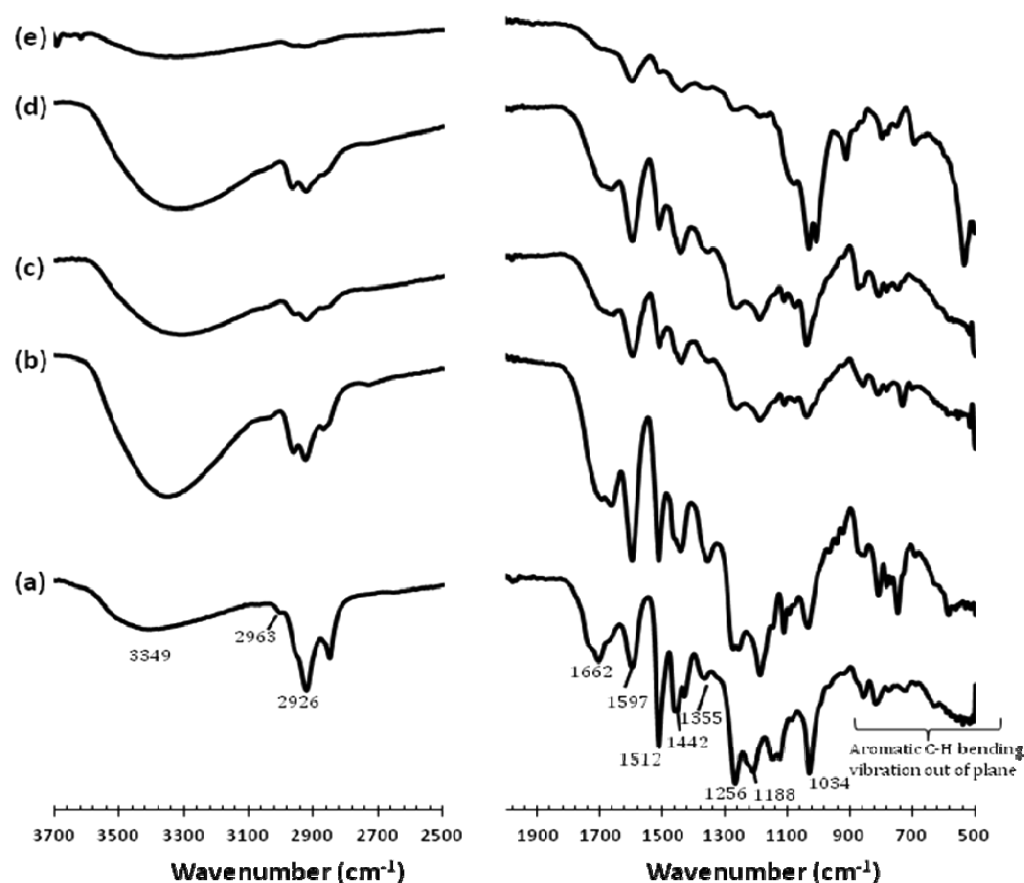
**Gel Permeation Chromatography (GPC).** Molecular weight data was determined by GPC. Samples were dissolved in THF (1:4 w/v, mg/mL), cotton-filtered, and injected without further treatment. The lignin samples were analyzed with a Polymer Laboratories GPC-50 (Varian, Inc.) and eluted at a flow rate of 1.2 mL min<sup>-1</sup> with THF on a column set made of two OligoPore GPC columns (particle size 6 μm, 300 × 7.5 mm) maintained at 35 °C. A differential refractometer index (RI) was used as detector. The molecular weight distribution was determined using an Integrated GPC system with CIRRUSTM GPC software based on a calibration curve pre-established with six polyethylene glycol/polyethylene oxide standards in the MW range of 106–12,140.

**Scanning Electron Microscopy (SEM).** Scanning electron microscopy (SEM) was run on a conductive carbon tape and sputter coated with gold using a JEOL JXA-840A scanning electron microscope equipped with an Oxford instruments 6560 INCA X-sight light element energy dispersive X-ray (EDX) spectrometer and digital image capturing software. The secondary electron photographs were taken using an accelerating voltage of 20 kV and a working distance of 10 mm. SEM images shown in this work were recorded at a magnification of 5000×.

**Thermogravimetric Analysis.** The TGA curves were obtained on a TGA Q series Q500-1708 equipped with TA universal analysis 2000. Freeze-dried lignin samples of 1.5 ± 0.1 mg were weighed in an aluminum pan. Measurements were carried out in an inert atmosphere. Starting with an isothermal for 10 min at RT under nitrogen atmosphere, temperature was raised to 100 °C, and an isothermal plateau was kept for 10 min to eliminate moisture that could initiate an oxygen-promoted decomposition of lignin. Then, after equilibrating at 50 °C with a scanning (heating and cooling) rate of 10 °C/min, a ramp to 600 °C was performed. Thermal degradation was observed within the temperature range of 50–600 °C.

## RESULTS AND DISCUSSION

Pyrolytic lignins were obtained from pyrolysis oils by water precipitation, followed by subsequent solvent extractions to yield four lignin fractions: methanol insoluble (MI), water insoluble (WI), and both dichloromethane immersed (DI) and



**Figure 1.** FTIR spectra of the lignins isolated from the pyrolysis oil and raw materials. (a) Extracted Etek lignin, (b) DS lignin, (c) WI lignin, (d) DI lignin, and (e) MI lignin.

soluble (DS) fractions. The most abundant of the fractions was the dichloromethane insoluble layer accounting for 50 wt % of the pyrolytic lignin. The chemically similar water immersed lignin was next most abundant at 28 wt %. The methanol insoluble accounted for 17 wt % of the material, and the DS material was the smallest fraction at only 5 wt % of the material. The extracted Etek lignin (EEL, used as the control) has been obtained as a fine homogeneous powder by THF extraction; the material was 12% of the total Etek lignin feedstock. Isolated lignins were characterized in terms of elemental composition (C, H, N, S, O), functional groups (ATR-FTIR and  $^{31}\text{P}$  NMR of derivatives), molecular mass characteristics (GPC), thermal stability (TGA), and surface morphology (SEM).

**Elemental Composition and Heating Values.** The elemental compositions of isolated lignins are given in Table 1 with the calculated heating values. The EEL and DS PL contain more carbon than the WI and DS PLs, with the MI fraction having the lowest carbon content due to its high inorganic (ash) content. Hydrogen content is higher in the nonthermally altered lignin than in any of the pyrolytic lignin fractions. Of the pyrolyzed lignins, the DS fraction had the highest hydrogen content at 6.3 wt %. The DI and WI PLs have similar hydrogen content at 5.4 and 5.8 wt %, respectively, while the MI PL had the lowest hydrogen value. Values of nitrogen content are negligible, and the sulfur content was below the detectable limit ( $<0.1\%$ ) for all of lignin fractions. The fact that values of oxygen content were slightly higher for the isolated PLs compared to the EEL suggests that more carbon and hydrogen than oxygen from lignin is lost to gases,

char, or small molecules in the PO during pyrolysis; this agrees with the functional group analysis discussed below. Heating values of isolated lignins ranged between 23.5 and 27.2 MJ/kg, except for the MI fraction that showed exceptionally low HHV at 9.7 MJ/kg, again due to its high inorganic content. The EEL, DS, WI, and DI PLs all have similar values, which match previous data.<sup>22</sup>

**FTIR Spectra Characteristics.** FTIR spectra of the five isolated lignins are presented in Figure 1. A tentative assignment to a guaiacyl (G) ring was made when a peak at  $1287\text{--}1270\text{ cm}^{-1}$  together with another at  $1142\text{--}1125\text{ cm}^{-1}$  were associated to a third observed at  $886\text{--}881\text{ cm}^{-1}$  (aromatic C–H in plane deformation). Comparison of the OH stretching region ( $3000\text{--}3600\text{ cm}^{-1}$ ) shows a marked difference in the intensities of the OH band. The DS PL exhibits the largest peak in this region, suggesting that it is the most hydroxylated of the lignins. All of the pyrolytic lignins except MI are more hydroxylated than nonthermally altered lignin. In addition, the C–H stretching region at  $\sim 2960\text{ cm}^{-1}$  indicates the presence of fewer methoxy groups in the PLs than in EEL. This decrease in the number of C–H bonds and increase in OH bonds in the PLs suggests that thermal degradation causes homolytic cleavage of the RC–OAr bond in aryl–O–alkyl etheric linkages, resulting in the formation of phenoxy radicals and therefore producing in a more phenolic product. Most of the cleaved methyl groups are terminated as methane or light hydrocarbons.

A comparative interpretation of features in the fingerprint region of the IR spectra reveals a guaiacyl (G) ring (C–O

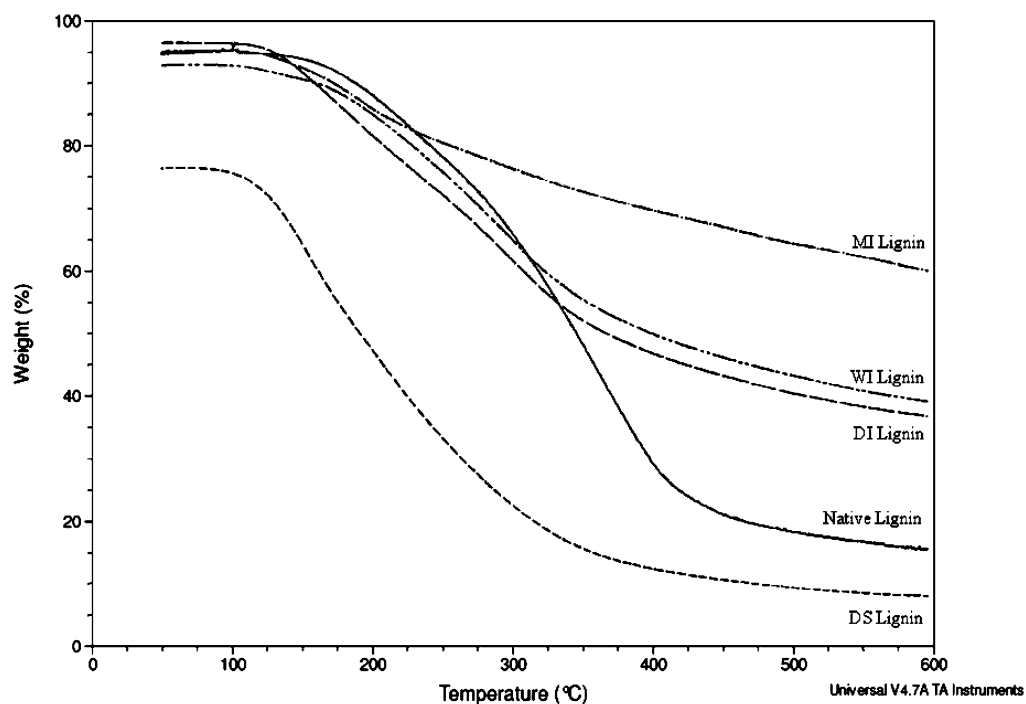


Figure 2. Thermogravimetric analysis graph of isolated lignins.

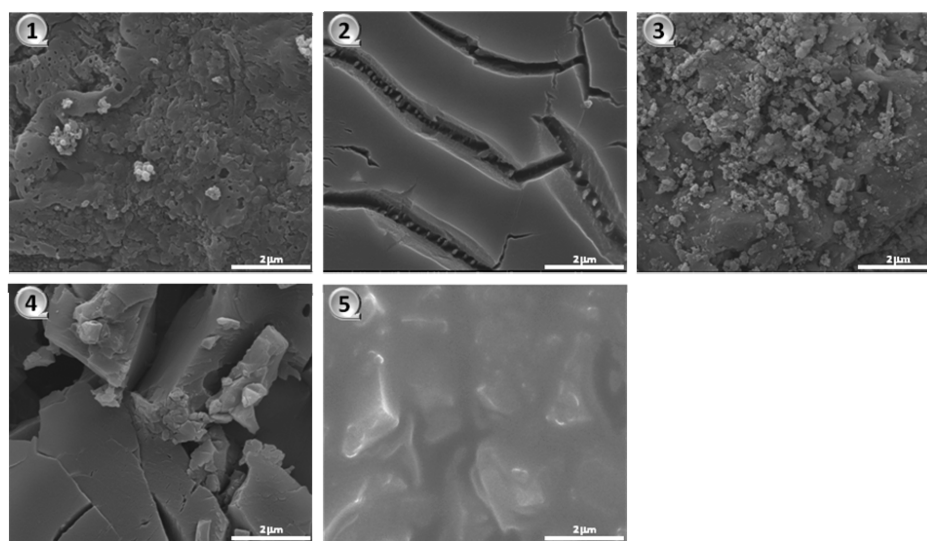


Figure 3. SEM images of isolated lignins. Micrographs 1, EEL; 2, DI lignin; 3, MI lignin; 4, WI lignin; and 5, DS lignin. With DI, dichloromethane insoluble; DS, dichloromethane soluble; MI, methanol insoluble; EEL, extracted Etek lignin; and WI, water immersed.

stretching at  $\sim 1263\text{ cm}^{-1}$ ) in the nonthermally altered lignin that was also observed in most PLs, except the MI fraction. A comparison of the  $\text{C}=\text{O}$  stretching bands ( $1650\text{--}1900\text{ cm}^{-1}$ ) shows that the DS lignin has a higher concentration of carbonyls than the DI and WI PLs, and this could explain the difference in their solubility in dichloromethane. Taken together, these results suggest that the DS fraction is the most hydroxylated and carbonylated PL, and therefore, might be the best feedstock for the production of functionalized chemicals through depolymerization.

**Thermal Stability.** To compare the stability of the isolated pyrolytic lignins, thermogravimetric analysis was performed. The thermogravimetric (TG) curves obtained at  $10\text{ }^\circ\text{C}/\text{min}$  heating rate are shown in Figure 2. Thermal degradation profile

of the nonthermally altered lignin started at  $145\text{ }^\circ\text{C}$  and was completed at  $550\text{ }^\circ\text{C}$ ; the typical weight loss accompanying this structural change was 5 wt % at  $100\text{ }^\circ\text{C}$ , 77 wt % at  $410\text{ }^\circ\text{C}$  (inflection of the TGA curve), and 88 wt % at the completion of the heating process. The PLs began decomposing at  $110\text{--}120\text{ }^\circ\text{C}$  and show different curvatures, most of them without a plateau. The lowest mass percent remaining at  $600\text{ }^\circ\text{C}$  (10%) was the dichloromethane-soluble PL. The TGA curves of the water and dichloromethane insoluble PLs were similar. Respectively, these exhibited a 92.5 and 95.5 wt % mass percent remaining at the initial degradation temperature ( $120\text{ }^\circ\text{C}$ ), inflections at 350 and  $345\text{ }^\circ\text{C}$  (55 and 57 wt %), and final weights of 40 and 38 wt % at  $600\text{ }^\circ\text{C}$ . The TGA curves suggest that both lignin fractions are chemically similar. The thermal

Table 2. Concentrations of Functional Groups and Molecular Weight Distribution of Isolated Lignins<sup>a</sup>

lignin sample	functional groups concentration (mmol/g)				average molecular weights		
	AlkOH	cond. PhOH	G–OH	COOH	$M_w$	$M_n$	PD
EEL	0.82	nd	1.16	0.25	854	531	1.62
MI lignin	0.91	nd	nd	0.08	212	206	1.03
WI lignin	1.24	0.58	3.30	0.09	383	336	1.14
DI lignin	1.44	0.52	3.01	0.10	430	355	1.23
DS lignin	0.81	0.5	3.81	0.11	399	343	1.22

<sup>a</sup>Quantitative <sup>31</sup>P-NMR determination of functional groups. AlkOH, aliphatic hydroxyl; cond. PhOH, condensed phenolic hydroxyl; G–OH, guaiacyl hydroxyl; and COOH, carboxylic groups.  $M_n$ , number average molecular weight;  $M_w$ , weight average molecular weight; and PD, polydispersity index.

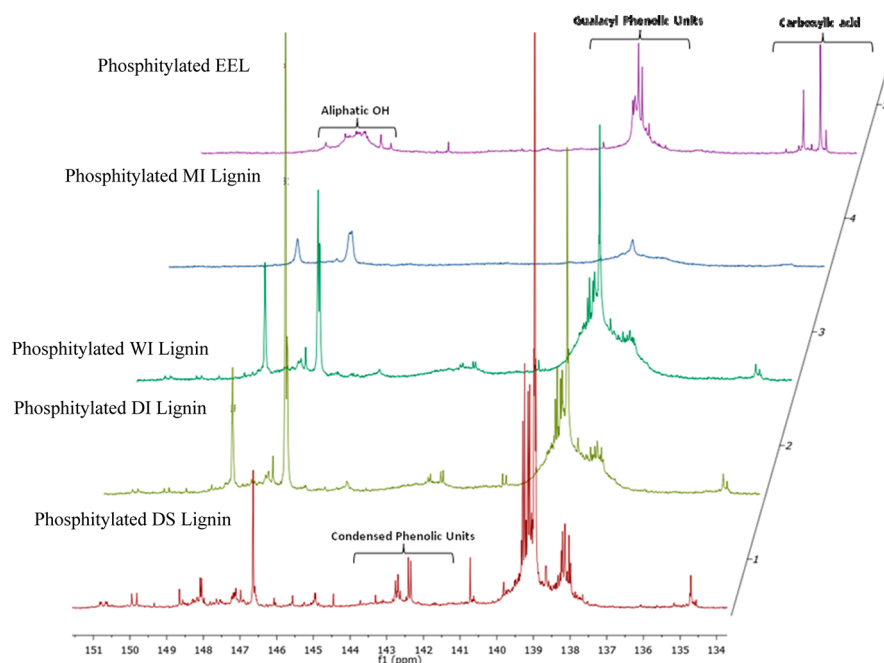


Figure 4. <sup>31</sup>P NMR spectra of phosphitylated isolated lignins.

decomposition of the pyrolytic lignins occurred slower over a broader temperature range than thermal decomposition of the nonthermally altered lignin. The DS lignin has a curve that matches most closely with the EEL, suggesting that it is the most similar to the original structure. The DI/WI fractions are more thermally robust than the EEL, which is to be expected for pyrolytic lignins as the weaker bonds are not likely to survive the pyrolysis. The TGA curves suggest that 110–120 °C temperature window is critical to the initiation of pyrolyzed lignin thermal decomposition.

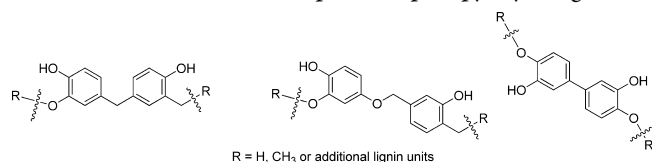
**Surface Morphology.** The use of the scanning electron microscopy (SEM) helped to visualize the thermal degrading effect of the pyrolysis treatment on the surface morphology of lignin granules. The SEM micrographs obtained at high magnifications (Figure 3) clearly showed that isolated lignins had different particle morphology in terms of shape and size of the granules. A closer look at the nonthermally altered lignin, i.e., the base-case (micrograph 1), showed a compact morphology with visible trenches having agglomerated light particles deposited on the surface of clusters. Those particles are reported<sup>23</sup> to be representative of some oxides (Na<sub>2</sub>O, K<sub>2</sub>O, SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>) or a complex of other inorganic material consisting of Mg, Ca, Fe, P, Ti, etc. Although they appear similar, the photomicrographs of the methanol-insoluble fraction (micrograph 3) differed from the native lignin in that

it displayed a dense microstructure with seldom trenches and numerous agglomerated small particles. This is typical of a lignin morphology that is highly degraded with high minerals content. The SEM image of the dichloromethane-insoluble lignin (micrograph 2) showed a splashed microstructure, but polygonal granules with fractal boundary edges were observed from the water-insoluble lignin (micrograph 4). Melting granules were also observed in the SEM of the dichloromethane-soluble lignin (micrograph 5).

**Molecular Weight.** The average molecular weights of isolated lignins are presented in Table 2, as weight average ( $M_w$ ), number average ( $M_n$ ), and polydispersity (PD). The average molecular weight of the nonthermally altered lignin (base case) is larger than that of each fraction of the pyrolytic lignins, confirming a thermal splitting of the biopolymer during the pyrolysis treatment, consistent with the <sup>31</sup>P NMR spectra (vide infra). The dichloromethane insoluble lignin exhibited the highest average molecular weight of the PLs, while the WI and DS fractions had molecular weights about 10% lower than the DI lignin. The observed PD values suggest that the solvent-guided isolation and fractionation procedure performed in this work allows for the isolation of PLs with relatively high homogeneity. Furthermore,  $M_w$  and  $M_n$  values of the nonthermally altered lignin match those reported on PLs elsewhere,<sup>24</sup> indicating that it is a structurally altered lignin due

to the highly acidic extracting conditions used industrially to produce fermentable sugars from woods and therefore is different from lignin found in unprocessed biomass.

**Functional Group Analysis via Phosphitylation and  $^{31}\text{P}$  NMR.** Figure 4 shows typical  $^{31}\text{P}$  NMR spectral profiles of phosphitylated lignins; the functional groups are tabulated in Table 2. An examination of the data reveals that aliphatic hydroxyl (0.82 mmol/g), guaiacyl phenolic hydroxyl (1.16 mmol/g), and carboxylic hydroxyl (0.25 mmol/g) groups have been observed from the spectrum of the nonpyrolyzed Etek lignin. As the later undergoes thermal pyrolysis, loss of carboxylic groups can be observed in the resulting pyrolytic lignins. The increased presence of free aryl (guaiacyl) hydroxyl groups indicates that cleavage of C–O bonds (mainly  $\alpha$ - and  $\beta$ -aryl) is occurring during thermal pyrolysis. Lignins are known to undergo condensation reactions due to high reactivity of the hydroxyl group of benzyl alcohols and may explain the observation of condensed moieties in the DS, DI, and WI PLs, which was not observed in the MI and nonpyrolyzed Etek lignins. Condensed lignin moieties consist of two aromatic rings with aliphatic links consisting of zero to two carbon–carbon or carbon–oxygen bonds; most native lignin structures have three-atom aliphatic links between aromatic rings. The presence of the condensed phenolic structures is the major structural difference between pre- and post-pyrolysis lignins.



Because the DS fraction is rich in these condensed moieties, it could be a source of chemicals with aromatic dimers of these types that could not be synthesized from nonthermally processed lignins. The DS, WI, and DI PLs represent lignin fractions with higher contents of guaiacyl phenol units, while high contents of aliphatic hydroxyls were seen on WI and DI lignins. A striking similarity between WI and DI lignins suggest that both fractions might be nearly identical. The fact that  $^{31}\text{P}$  NMR results show a higher content of guaiacyl phenolic units in the DS, DI, and WI lignins suggests more free phenolics containing etherified Ar–O bonds could be a target for chemical products from a pyrolysis oil based biorefinery.

## CONCLUSION

The lignin isolation method performed in this work produced pyrolytic lignins of relatively high homogeneity, with indication that the thermal splitting of the Etek lignin produced lignin fragments of lower molecular weight units. Fast pyrolysis of Etek lignin yields highly oxygenated components, which represent good starting materials for producing lignin-derived chemicals. The guaiacyl ring was kept in most pyrolytic lignins, suggesting that the thermally degraded lignins conserved some etherified bonds that might be targeted for further catalytic depolymerization to aromatic monomers. Furthermore, separation by solvent extraction of the isolated materials revealed that most of the material was not soluble in dichloromethane (~5 wt %). Condensed phenolic units represented the largest structural change between pre- and post-pyrolyzed lignins. Each fraction retained a large number of guaiacolic rings, suggesting that they could be a feedstock for chemicals of these types via further chemical depolymerisation. For further chemically selective conversion processes, isolated lignins should not be

used over 120 °C because nonselective thermal degradation can occur around this temperature.

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### Notes

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The authors declare no competing financial interest.

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